

PATENT SPECIFICATION

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(54) ELECTRODEPOSITED COMPOSITE COATINGS

(71) We, BRISTOL AEROJET LIMITED, a Company registered under the Laws of Great Britain, of Banwell, Weston-super-Mare, Somerset, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electrodeposited composite coatings, i.e. coatings which consist of an electrodeposited metal matrix with included particles which are codeposited with the matrix. The particles are suspended in the electrolyte containing the metal ions for the matrix and are substantially insoluble in the electrolyte and, during the plating operation, become included in the plated matrix.

It has already been proposed to employ various metals as the matrix, for example nickel and copper, and it has also been proposed to employ various particles, for example alumina and graphite. However, the coatings of the present invention are believed to have a wear resistance which is better, and surprisingly better, than the coatings hitherto proposed.

According to one aspect of the present invention, an electrodeposited composite coating comprises, as deposited, a matrix which is at least 50% by weight cobalt and particles included in the matrix which are at least 50% by weight chromium carbide, at least 50% by weight of the particles having a particle size of less than ten microns and preferably between 2 and 5 microns.

The particles will normally be present in the coating, as deposited, in an amount of less than 50% by weight, and in most cases less than 40% by weight. Although, as deposited, all the particles may be wholly chromium carbide, there may be a minor proportion by weight of other particles; for example, there may be 5% by weight of tungsten carbide particles. Although preferably all the particles have a size between 2 and 5 microns, it may not be practicable completely to avoid a small quantity of fines below 2 microns

and possibly some larger particles due, for example, to agglomeration. However, preferably more than 80% by weight of the particles lie within the specified limits.

The coatings may be applied to a variety of components subjected to wear such as aero-engine components, particularly those likely to operate at elevated temperatures, bearing surfaces, rocket nozzles, and tubes and nozzles carrying abrasive substances. The coatings may be applied to the whole component but more frequently they will be applied to only a portion of its surface. The electrodeposition technique is particularly suitable to the protection of selected areas and the coating of complex, re-entrant and inaccessible areas do not present any great problems.

It has been found by means of extensive tests that coatings in accordance with the invention have markedly better wear resistance, particularly at elevated temperatures, than other electrodeposited composite coatings which would be expected to have a very similar wear resistance.

The wear resistance properties are markedly improved by heating and preferably, therefore, the coatings are subjected to heat treatment before use or are applied to components which will be used in such a manner that at least the region of the coating close to the surface of the coating will be heated during use. If heat treatment is employed the coating is preferably held at a temperature above 500°C for a period in excess of two hours, the preferred ranges being between 850°C and 1100°C for a period of between two and twenty-four hours. The heating may be followed by a water or oil quench. Alternatively or in addition, the coating may be subjected to some form of working such as grinding and lapping which raises the temperature of the region of the coating close to the surface, for example, at least two Angstroms of thickness, sufficiently to enhance the wear resistance properties of the coating.

Where the coating is used for a component which in use becomes heated because of fric-

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tion, e.g. as a bearing surface, a heat treatment either by furnace or by working may be carried out during the course of manufacture as mentioned above or may be unnecessary depending upon the particular use. Where there is no manufacturing heat treatment it may, in some cases, be desirable to use the coating under no load or light load conditions for an initial period during which the wear resistance properties of the coating are enhanced by the heat generated by friction before the component is subjected to full load conditions. Thereafter, as material is slowly removed from the surface by wear the underlying layers will be successively heated so that the surface will always be afforded by a heat treated layer.

It is believed that the unexpectedly good wear resistance properties possessed by the heat treated coatings of the invention are due to three factors. The first of these is that during heat treatment there is diffusion of cobalt into the chromium carbide particles thus producing particles of cobalt, chromium and carbon in a cobalt matrix. It is possible that there is some slight diffusion of chromium and carbon into the cobalt but tests indicate that this is very slight if it occurs at all. This diffusion of cobalt into the carbide particles can occur readily in an electrodeposited composite because there are substantially no oxide films around the particles and complete metallurgical 'wetting' takes place. The diffusion of cobalt into the chromium carbide preferably produces an increase in the total volume of the particles in the coating of at least 50% and has been found in some cases to increase the size of the particles by as much as 100% in volume, thus greatly increasing the proportion of hard particles in the coating, and it is believed that the particles now consist largely of a complex chromium-cobalt-carbide. In addition to the effect produced merely by the increased proportion of carbide present in the composite coating, the increase in particle size resulting from the diffusion of cobalt into the particles causes the particle boundaries to migrate so that a new interface is formed which is clean and strong.

The second factor which enhances the properties of the coatings which have been heat treated is that the cobalt matrix is modified. The cobalt as deposited is in the close-packed hexagonal form with a very high energy state. At temperatures above 417°C cobalt changes to a face-centred cubic form and it is probable that almost all of the f.c.c. form is retained on subsequent cooling whether slow or rapid. The effect of heat treatment is therefore to reduce the energy level of the as-deposited cobalt.

The third factor is that heat treatment produces an increase of grain size of the cobalt matrix. The second and third factors combine to change a matrix which is brittle and

which tends to break like glass with separation occurring between the matrix and the particles in the region of fracture to a matrix which is tough and ductile, the line of fracture when the coating is broken passing through both matrix and particles.

A further effect of heat treating is that some, at least, of the particles which originally were in the form Cr_3C_2 are transferred to the M_3C_2 form, where M represents both cobalt and chromium since both are present in the complex carbide which is produced by heat treatment.

Thus, according to another aspect of the present invention, an electrodeposited composite coating, wherein diffusion has occurred within the coating, comprises a matrix which consists wholly or contains at least 90% by weight of cobalt and particles included in the matrix which particles comprise a complex chromium-cobalt-carbide. Preferably the particles are present in an amount of between 30% and 65% by volume. The lower limit is preferably 40%.

Electrodeposition may be carried out using a standard plating bath containing the chromium carbide particles dispersed through the electrolyte. Various means may be used to maintain the particles in homogeneous suspension by two preferred means will now be described with the accompanying drawings, in which:

Figure 1 is a diagrammatic view of the first form of the apparatus;

Figure 2 is a side elevation of the second form of the apparatus; and

Figure 3 is a fragmentary section on the line III—III in Figure 2.

The apparatus shown in Figure 1 of the drawing comprises a container 1 of circular cross-section having a conical bottom section 2 which is connected to a peristaltic pump 3 by a feed tube 4. A suction tube 5 has its free end 6 dipping into the plating solution 7 in the container 1 and leads to the suction inlet of the pump 3. A branch pipe 8 having an open upper end above the surface 9 of the solution 7 opens into the pipe 5.

A pure cobalt anode 11 dips into the solution 7 adjacent the side wall of the container and the component 12 to be coated is suspended in the centre of the container 1 as the cathode. The anode and cathode are connected to a 15 volt supply.

The process is carried out as follows. The plating solution with the appropriate proportion of solid particles is placed in the container and the pump 3 is started. This withdraws solution through the pipe 5 and returns it to the container at the bottom of the conical portion 2. Air is drawn in through the branch pipe 8 and is delivered with the solution to the container. The pump therefore produces a continuous circulation of solution and produces a flow of air bubbles upwards through

the solution in which the article to be coated is suspended. This tends to maintain the particles evenly distributed through the solution in the container and tends to prevent the formation of large agglomerations of particles. The rate of circulation, which can be adjusted by altering the speed of the pump 3, and the proportion of air drawn in, which can be adjusted by altering a restriction at the upper end of the branch pipe 8, are selected to give the rate of circulation which approximately balances the gravitational forces on the particles in the container so that the particles in the container are maintained in suspension and either rise or fall in the solution quite slowly.

The apparatus shown in Figures 2 and 3 comprises a rectangular tank 11a containing a bath of plating solution 12a and particles which are to be codeposited. In the tank 11a there is a plate agitator 13 having perforations 15 (Figure 3) through it. At the central point 14 of each of two opposite sides the plate agitator is attached to one arm 16 of an inverted U-shaped member 17, one arm 16 of which is within the tank and the other arm 18 is outside the tank. The inverted U-shaped members 17 are arranged to reciprocate in a vertical direction so as to reciprocate the perforated agitator plate 13 in the region adjacent the bottom of the container between the position shown in dotted lines in Figure 2 and a position below the area in which deposition takes place. The distance moved by the agitator plate is conveniently about $\frac{1}{3}$ the depth of the bath. The U-shaped members 17 are guided in brackets 21 situated outside the tank and rigidly attached to a cylinder 22. Attached to the arm 18 of the U-shaped member 17 is a yoke 23 which is also attached to a piston rod 24 of a piston 25 which reciprocates within the cylinder 22. Reciprocation of the piston and piston rod, therefore, causes the U-shaped member and the agitator plate to reciprocate. The movement of the pistons is controlled by means which are not shown.

An anode 24 dips into the solution 12a adjacent one side wall of the tank and the components to be coated are suspended adjacent the centre of the bath as the cathode. The anode and the cathode are connected to an electricity supply via control equipment

of the kind normally employed for plating.

The process is carried out as follows. When plating is to take place, reciprocation of the plate 13 by the piston is begun. Thus the plate sweeps approximately the bottom third of the bath which produces vigorous agitation of the solution as it is forced through the perforations 15 and the narrow clearances between the edges of the plate and the walls of the tank. The particles are, therefore taken into suspension. When the solution has been agitated for a sufficient time for it to become homogeneous the components to be plated are loaded into the bath and the plating current is switched on and plating proceeds in the normal way. Reciprocation of the plate 13 is continued throughout the plating operation to maintain the homogeneity of the solution.

Electrolytic composite deposition preferably occurs at a current density in the range of 1 to 7 amps per square decimetre of area being plated with a preferred value of 4 a/dm². Currents in this range have been found to produce deposits ranging from 19% to 29% volume content of chromium carbide which are satisfactory levels. A current density much below 1 a/dm² produces a deposit with an insufficient quantity of particles while much above 7 a/dm² the deposit tends to be unacceptable because of nodular edge growth.

It has been found that satisfactory deposition occurs if the pH of the plating bath is maintained between 3.25 and 5.5 with a preferred value of pH 4.7.

Best results are obtained if the temperature of the plating bath is maintained between 20°C and 65°C with an optimum value of about 50°C.

The concentration of carbide particles in the electrolytic bath affects the proportion in the deposited coating and should preferably not be below 300 grams per litre. It is found that increases in concentration much above 550 g/l produce little increase in the proportion of particles in the deposited coating. The preferred concentrations 500 g/l.

The invention will be illustrated by the following Example.

A test piece of steel was coated in the apparatus shown in Figures 2 and 3. The tank contained an electrolytic bath of the following composition:

Cobalt sulphate (CoSO₄ · 6H₂O)
Sodium chloride (NaCl)
Boric acid (H₃BO₃)

40 oz/gal (250 g/l).
2½ oz/gal (16 g/l).
5 oz/gal (31 g/l).

The bath also contained 500 g/l of chromium carbide (Cr_3C_2) powder having a particle size of 2 to 5 microns mean particle diameter. The bath had a pH of 4.7 and during deposition it was maintained at a temperature of approximately 50°C .

The test piece was first degreased in trichlorethylene vapour and was then shot blasted with grade 50μ alumina shot at a working air pressure of 75 pounds per square inch. The agitator in the bath was then switched on and when the particles had become distributed through the bath the test piece was connected to the current supply as the cathode and was inserted in the bath. The current was adjusted to give a density of 4 a/dm². After a time sufficient to produce a coating thickness of 125μ the test piece was removed from the bath and was washed and dried. Part of the test piece was then examined in the optical microscope and the micrograph shown in Figure 4 was obtained at 1000 fold magnification. This shows discrete chromium carbide particles in the cobalt matrix.

The test piece was then heat treated by being maintained at a temperature of $1,000^\circ\text{C}$ for four hours followed by an oil quench. Part of the test piece was again examined microscopically and the micrograph shown in Figure 5 was obtained at 1000 fold magnification. It will be seen that the particles have become enlarged and have tended to

coalesce. As mentioned above, this is due to diffusion of cobalt into the carbide particles. It was found that the diamond pyramid microhardness had risen from 465 ± 10 to 600 ± 20 .

Similar test pieces were produced using a similar bath but with particles of tungsten carbide and silicon carbide respectively.

The test pieces were then tested for wear at temperatures between 200°C and 700°C against four materials commonly employed in the manufacture of aero engines. These materials were the alloy known as Nimonic 80A (N 80A), a nickel base casting alloy designated C 242, a cobalt base alloy known by the trade name Haynes 25 and the 12% chromium steel designated S/SJ2. NIMONIC is a Registered Trade Mark. The wear tests were carried out in a wear testing machine which reciprocates a spherical specimen to be tested on a plane surface of the other material of the couple under a constant load and with constant stroke length for a predetermined number of cycles. Wear is ascertained by direct measurement of the wear scars produced on the test specimen and the other material of the couple and is expressed in volume lost. The results of the tests are given in the following Table and it will be seen that at temperatures of 300°C and upwards, the coatings containing chromium carbide have a very considerable superiority over those containing tungsten carbide and silicon carbide.

TABLE

Wear Couple (Total Wear)		Temperature Degrees Centigrade					
		200	300	400	500	600	700
		Sum of Volume of Material Removed $\times 10^{-6}$ cu. ins. from each face					
Cobalt-chromium carbide	N80A	33.9	1.5	0.58	3.22	0.92	0.41
Cobalt-tungsten carbide	N80A	40.1	13.26	5.61	7.52	1.13	—
Cobalt-silicon carbide	N80A	49.6	77.1	14.67	17.15	23.10	—
Cobalt-chromium carbide	C242	39.1	0.97	0.56	2.19	0.40	0.31
Cobalt-tungsten carbide	C242	28.3	45.1	14.89	18.80	—	—
Cobalt-silicon carbide	C242	44.9	34.4	8.61	3.51	1.03	0.40
Cobalt-chromium carbide	H25	38.85	0.97	0.10	0.57	0.45	0.10
Cobalt-tungsten carbide	H25	51.70	35.60	49.10	12.20	—	—
Cobalt-silicon carbide	H25	No results due to specimen damage					
Cobalt-chromium carbide	S/SJ2	44.95	2.43	0.48	0.40	0.72	12.45
Cobalt-tungsten carbide	S/SJ2	32.8	51.95	43.87	2.20	0.17	—
Cobalt-silicon carbide	S/SJ2	36.7	41.9	12.05	1.67	2.78	—

The apparatus shown in Figure 1 is also described and shown in our Patent No. 1,218,179 which claims a process for the electrodeposition of a composite coating comprising a metal matrix containing particles in which process the particles are co-deposited with the metal from a solution in which the particles are insoluble, and in which process the solution is circulated through the container in which electrodeposition takes place, gas being admitted to the container to produce a generally upward flow of solution and gas in the vicinity of the surface on which deposition is occurring.

The apparatus shown in Figures 2 and 3 is also described and shown in our Patent No. 1,329,081 which claims, according to one aspect, apparatus for the electrodeposition of composite coatings consisting of a metal matrix with particulate additions, the apparatus including a container for the electrolyte and the particles, an electrode in the container, an electrical connection to the electrode, a generally horizontal perforated agitator in a region adjacent the bottom of the container, and means for reciprocating the agitator in a vertical direction; the Patent also claims, according to a second aspect, a method of producing composite coatings consisting of a metal matrix with particulate additions, in which method electrolytic deposition of metal takes place in a solution which contains insoluble particles, the solution being agitated by movement generally up and down of a generally horizontal perforated agitator in a part of the solution below and spaced from the part used for deposition.

WHAT WE CLAIM IS:—

1. An electrodeposited composite coating comprising, as deposited, a matrix which is at least 50% by weight cobalt and particles included in the matrix which are at least 50% by weight chromium carbide, at least 50% by weight of the particles having a particle size of less than ten microns.
2. A coating as claimed in Claim 1 in which at least 50% by weight of the particles have a particle size, as deposited, of between two and five microns.
3. A coating as claimed in Claim 2 in which more than 80% by weight of the particles have a particle size, as deposited, of between two and five microns.
4. A coating as claimed in any of the preceding claims which, after deposition, has been treated to produce diffusion of cobalt into the carbide particles.
5. A coating as claimed in Claim 4 in which the coating contains between 30% and 65% by volume of carbide particles.
6. An electrodeposited composite coating, wherein diffusion has occurred within the coating, comprising a matrix which contains at least 90% by weight of cobalt and particles included in the matrix which particles com-

prise a complex chromium-cobalt-carbide.

7. A coating as claimed in Claim 6 in which the particles are present in an amount of between 30% and 65% by volume.

8. A coating as claimed in Claim 6 or Claim 7 in which the particles are present in an amount of at least 40% by volume.

9. A coating as claimed in Claim 6 or Claim 7 or Claim 8 in which some of the particles are present in the form M_7C_3 where M represents both cobalt and chromium.

10. A method of producing a coating which comprises electrodepositing a matrix of cobalt and codepositing with the matrix particles suspended in the electrolytic bath the particles being at least 50% by weight chromium carbide, at least 50% by weight of the particles having a particle size of less than ten microns.

11. A method as claimed in Claim 10 in which at least 50% by weight of the particles have a particle size between two and five microns.

12. A method as claimed in Claim 11 in which more than 80% by weight of the particles have a particle size between two and five microns.

13. A method as claimed in Claim 10 or Claim 11 or Claim 12 in which the deposited composite coating is heat treated to produce diffusion of cobalt into the carbide particles.

14. A method as claimed in Claim 13 in which the heat treatment comprises maintaining the coating at a temperature above 500°C for a period in excess of two hours.

15. A method as claimed in Claim 13 or Claim 14 in which the heat treatment produces an increase in the total volume of the particles in the coating of at least 50%.

16. A method as claimed in Claim 11 or Claim 12 or Claim 13 in which a surface of the coating is subjected to working so as to produce diffusion of cobalt into the carbide particles in a surface layer of a thickness of at least two Angstroms in which the volume of the carbide particles is increased by at least 50%.

17. A method as claimed in any of Claims 10 to 16 in which the process is performed in a bath from which solution is withdrawn and returned to the bath in a region lower than that from which it was withdrawn and in which gas is admitted to the lower region of the bath to maintain the particles in suspension.

18. A method as claimed in any of Claims 10 to 16 in which the process is performed in a bath which is agitated by the movement generally up and down of a generally horizontal perforated agitator plate in the part of the bath below the part used for deposition.

19. A method as claimed in any of Claims 10 to 18 in which deposition is carried out at a current density in the range of 1 to 7 amps per square decimetre.

20. A method as claimed in any of Claims 10 to 19 in which deposition is carried out in a bath having a pH between 3.25 and 5.5.
- 5 21. A method as claimed in any of Claims 10 to 20 in which deposition is carried out in a bath at a temperature between 20°C and 65°C.
- 10 22. A method as claimed in any of Claims 10 to 21 in which deposition is carried out in a bath containing between 300 and 550 grams per litre of chromium carbide particles.
23. A method of producing a coating substantially as described in the foregoing Example.
24. A coating when produced by a method as claimed in any of Claims 10 to 23. 15

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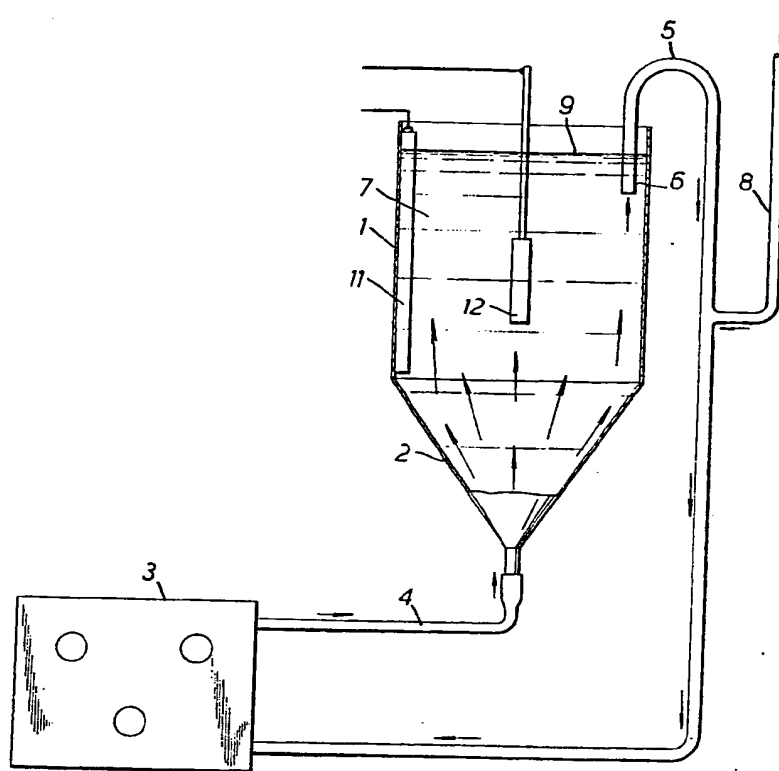


FIG. 1.

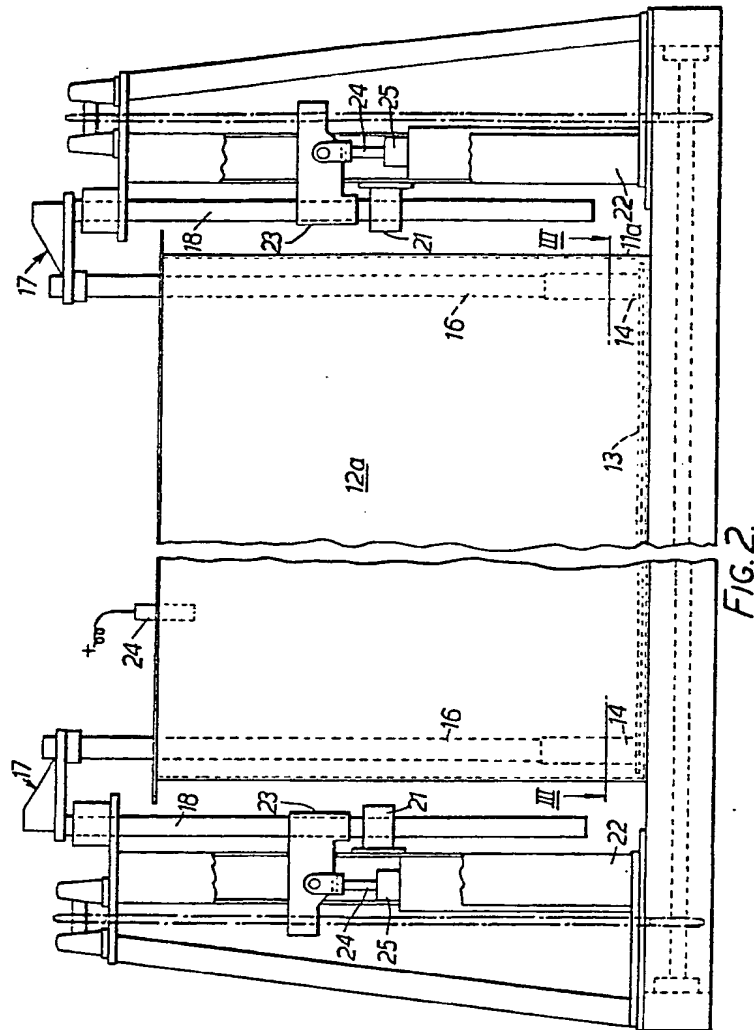
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Sheet 2



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Sheet 3

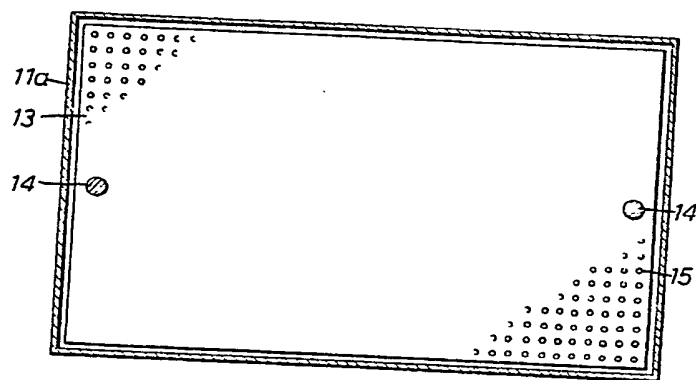


FIG. 3.

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Sheet 4

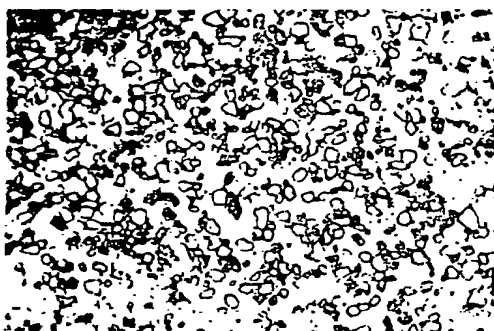


FIG. 4.

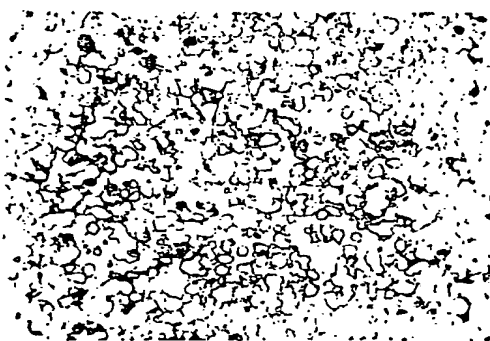


FIG. 5.

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